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Conjugated Oligothienyl Dendrimers Based on a Pyrazino[2,3-*g*]quinoxaline Core

Michael Mastalerz,*,† Viktor Fischer,† Chang-Qi Ma,† René A. J. Janssen,‡ and Peter Bäuerle*,†

Institute of Organic Chemistry II and Advanced Materials, Ulm University, Albert-Einstein-Allee 11, 89081 Ulm, Germany, and Molecular Materials and Nanosystems, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

peter.baeuerle@uni-ulm.de; michael.mastalerz@uni-ulm.de

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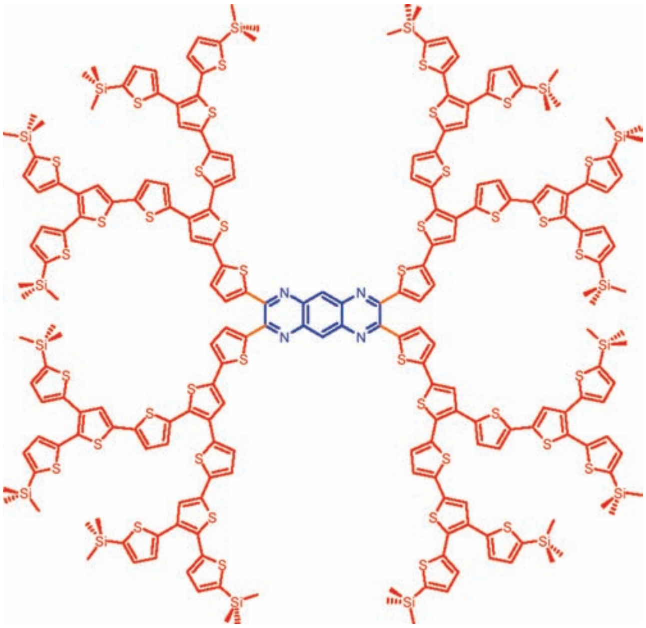
ABSTRACT



The synthesis of a new series of conjugated dendrimers based on an electron-accepting core is introduced. The compounds showed broad absorption bands over 300−700 nm and have reduced HOMO−LUMO gaps of 1.7−1.9 eV. Incorporation of these compounds in bulk heterojunction solar cells as electron-donating material along with $PC_{61}BM$ as electron acceptor gave power conversion efficiencies of up to 1.3% for the second-generation dendrimer.

Within the family of shape-persistent molecules, π-conjugated dendrimers represent a new class of well-defined structures with the potential for organic electronic applications,[1] such as organic light emitting devices (OLEDs),[2] organic field effect transistors (OFETs),[3] or organic photovoltaics.[4,5]

Recently, we showed that defined dendritic conjugated oligothiophenes (DOT) perform well in bulk heterojunction solar cells (BHJSC) with [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$), giving overall performances η of up to 1.7% and higher open circuit voltages V_{oc} ($\leq$1 V)[5] than cells with the standard combination poly-3-hexylthiophene (P3HT)/$PC_{61}BM$.[6]

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† Ulm University.
‡ Eindhoven University of Technology.

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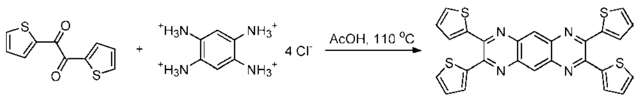
The purpose of our recent work is to develop DOTs which could “harvest” more of the sunlight by extending the absorption of the dendrimers to longer wavelengths. Inspired by the good performances of low band gap polymers,[7] we combined electron-accepting and -donating subunits in DOT structures.[8] In this respect, we developed perylene bisimide−DOT hybrids[8a] or pyridine− and pyridinium−DOT combinations.[8b] The latter class of compounds showed moderate efficiencies in BHJSCs with PC$_{61}$BM ($\eta < 0.5\%$), but more important was the contribution of a longest wavelength charge-transfer band to the internal photon to current efficiency (IPCE). Besides our approaches in the field of dendritic conjugated structures, Roncali and co-workers demonstrated a similar donor−acceptor approach on π-conjugated star-shaped molecules, giving power conversion efficiencies of up to 1.2%.[9]

Herein, we now present the synthesis of a new class of acceptor-functionalized conjugated dendrimers, where the electron-accepting core is represented by a pyrazino[2,3-*g*]quinoxaline (PQ).[10] This PQ-core is fully conjugated to the DOT moieties, and consequently, a bathochromic shift of the absorption and a reduced band gap with respect to the all-thiophene DOTs[5] is expected.

It is well-known that pyrazine units can be generated through condensation of 1,2-diketones and 1,2-diamines.[11] In this manner, we synthesized tetrathienyl-PQ **3** in 39% yield from commercial available starting materials **1** and **2** (Scheme 1). However, compound **3** showed a very low solubility in common organic solvents and had to be extracted via Soxhlet extractor. Despite the low solubility, the compound showed promising photophysical properties (see discussion below). The next step of our synthetic route was to introduce the PQ-core to a DOT structure. Therefore, we first synthesized dibrominated 1,2-diketone **4** in 56% yield through a bromination of **1** with bromine and sodium bicarbonate in chloroform (Scheme 2).[12] Subsequent Suzuki−Miyaura cross-coupling reaction of **4** with terthienyl boronic acid **5**[5] gave diketone **6** in 77% yield. Unfortunately, condensation reaction of diketone **6** with tetraammonium salt **2** failed under various conditions: The only reaction that was observed was desilylation of the diketone.

Scheme 1. Synthesis of Generation Zero PQ **3**



1 **2** **3** (39%)

However, to circumvent this synthetic problem, we first condensed dibromo diketone **4** with tetraammonium benzene **2** to get tetrabromo compound **8** as the central building block. Surprisingly, this derivative was much more soluble in dichloromethane than **3** and could easily be purified by column chromatography, yielding an orange powder in 48% yield (Scheme 2). A subsequent palladium-catalyzed cross-coupling of **8** with 3T-boronic ester **5** gave DOT-PQ dendrimer **7** in 91% yield after size-exclusion chromatography. Reaction of **8** with 9T-dendritic boronic ester **9**[5]

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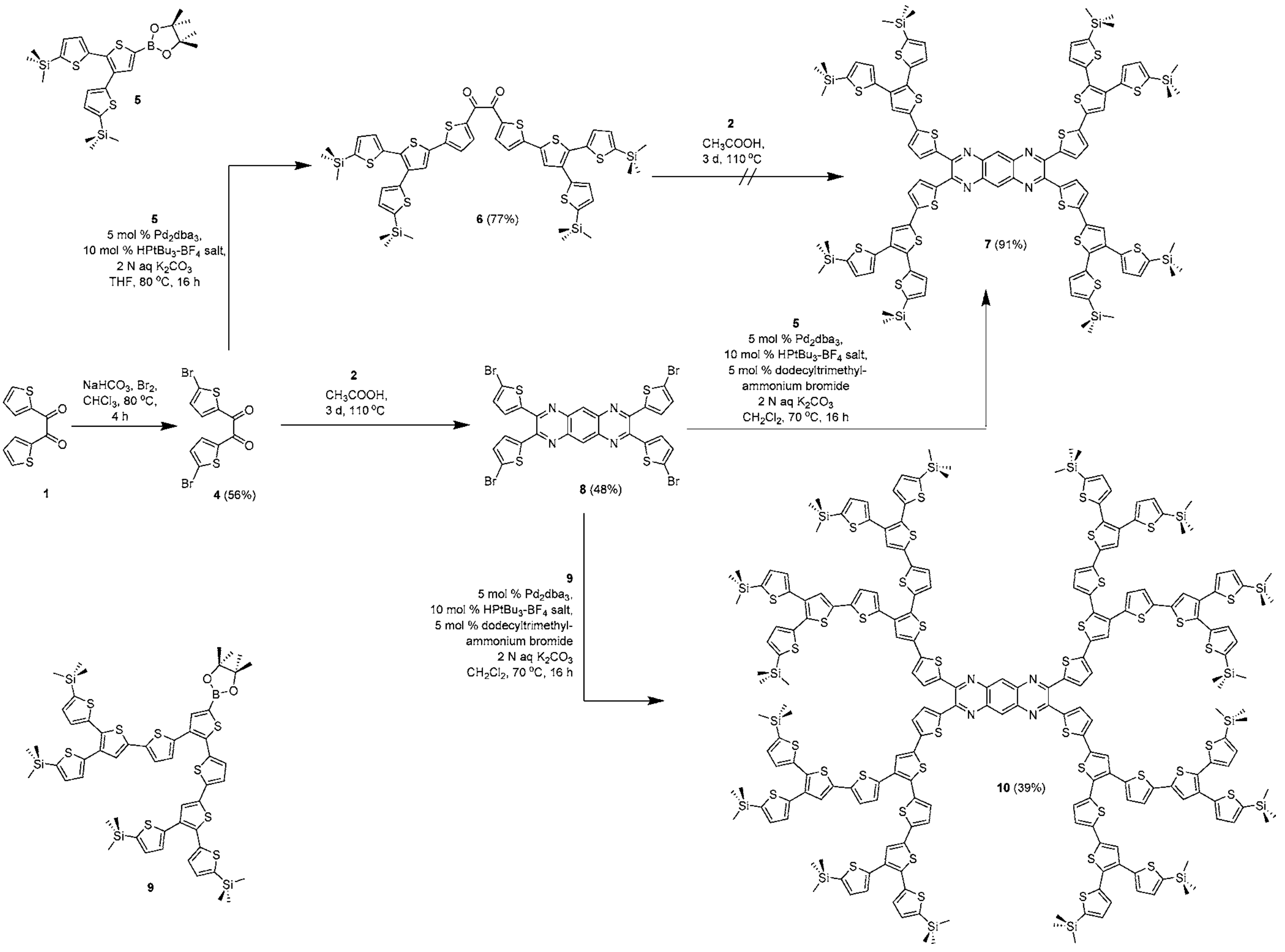
Scheme 2. Synthetic Routes to DOT-PQ Dendrimers **7** and **10**



resulted in second-generation DOT-PQ dendrimer **10** in somewhat lower yield (39%). In this case, a final purification step by recycling GPC was performed. Both dendrimers are dark green microcrystalline solids.

For the characterization of optoelectronic properties, first, UV/vis spectra in dichloromethane were recorded (Figure 1).

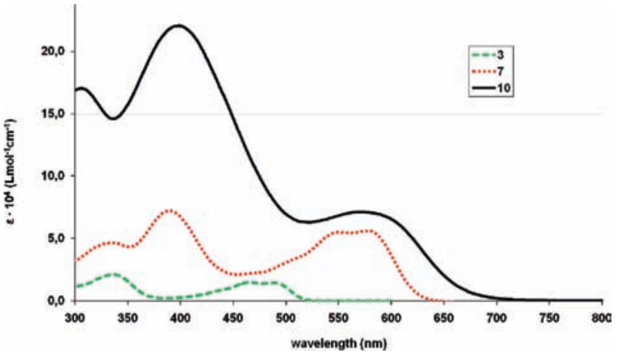


Figure 1. UV/vis spectra of PQ **3** and DOT-PQs **7** and **10** in dichloromethane.

Quinoxaline **3** showed a broad band with maxima at 488 and 466 nm and a second blue-shifted band at 337 nm. From the onset of the absorption spectrum an optical HOMO−LUMO gap of $E_g = 2.4$ eV was estimated. The absorption behavior of DOT-PQ dendrimer **7** was similar, but the bands were red-shifted (λ = 576, 545, and 398 nm) and more intense. By measurements of UV/vis spectra of **7** in various solvents of different polarity, we would rather assign the longest wavelength to $\pi-\pi^*$ transitions than to charge-transfer transitions between donor and acceptor units. The optical band gap is estimated to $E_g = 1.9$ eV.

The absorption behavior of second-generation DOT-PQ dendrimer **10** confirmed the trend and showed increased nonstructured broad bands with maxima at $\lambda_{max} = 570$ and 401 nm. Due to the broadness and tailing of the low energy band a gap of $E_g = 1.7$ eV was determined. Thus, as a consequence of the donor−acceptor character of these novel systems we find a successive shift of the longest wavelength bands and consequently

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(12) A synthetic approach to compound **4** via the Benzoin reaction has been previously described (26% yield): Hyatt, J. L.; Stacy, V.; Wadkins, R. M.; Yoon, K. J. P.; Wierdl, M.; Edwards, C. C.; Zeller, M.; Hunter, A. D.; Danks, M. K.; Crundwell, G.; Potter, P. M. *J. Med. Chem.* **2005**, *48*, 5543–5550.

the lowering of the HOMO−LUMO gap with increasing size of generation and of the oligothiophene dendrons.

Second, for the determination of HOMO−LUMO levels, which are important for application in solar cells, cyclic voltammetry (CV) was performed on DOT-PQs **7** and **10** (see the Supporting Information).[13] The measured redox potentials were transformed in energies vs vacuum and are displayed in Figure 2 relative to PEDOT:PSS and $PC_{61}BM$ which are typically used as hole transport layer and n-type acceptor, respectively, in BHJSCs. Both dendrimers **7** and **10** showed the propensity of a p-type semiconductor and had HOMOs more negative with respect to the HOMO of PEDOT and LUMOs sufficiently positive with respect to the LUMO of $PC_{61}BM$,[7a] guaranteeing effective electron transfers in BHJSCs. The relative trend of the HOMO/ LUMO levels in **7** and **10** well follows the optical data as the HOMO is destabilized with increasing size of the dendrimer and the LUMO stabilized oppositely.

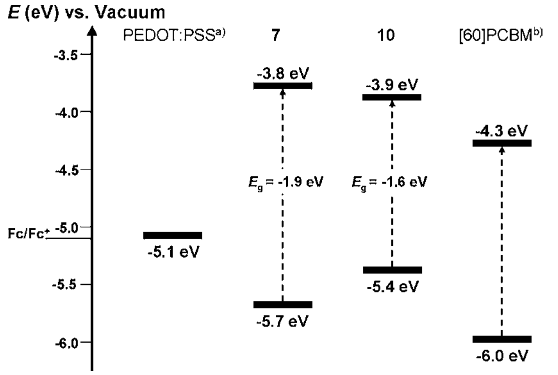

Figure 2. Energy level diagram for novel DOT-PQ dendrimers **7** and **10** in comparison with PEDOT:PSS and $PC_{61}BM$. Values taken (a) from the product information for Clevios P VP Al4083 and (b) from ref 7a.

We tested blends of donor−acceptor dendrimers **7** and **10** with $PC_{61}BM$ in a 1:3 ratio (w/w) in BHJSCs. Under AM1.5G illumination the device containing **7** as p-type material led to an open circuit voltage of $V_{OC} = 0.82$ V, a current density of $J_{SC} = 2.5$ mA/cm^2, and a fill factor of 0.32. The power conversion efficiency resulted to $\eta = 0.7\%$. Devices containing second-generation DOT-PQ **10** gave an excellent open circuit voltage of $V_{OC} = 1.00$ V and a higher current density ($J_{SC} = 3.3$ mA/cm^2), fill factor (0.38), and power conversion efficency (1.3%). Corresponding J−V curves are shown in Figure 3a. The spectral response (external quantum efficiencies) of the devices for both dendrimers clearly demonstrated the contribution of all absorption bands to the charge generation (Figure 3b). In comparison to **10**, the structurally closest TMS-protected all-thiophene dendrimer **42T-Si** gave a lower power conversion efficiency ($\eta = 1.0\%$).[5] These results demonstrate that the concept of low band gap materials here realized by a structurally defined donor−acceptor dendrimer can be beneficial for the performance of BHJSC devices.

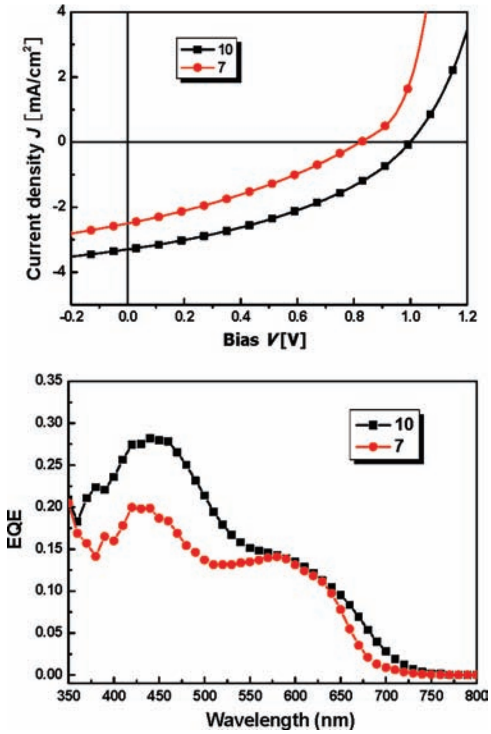

Figure 3. J−V (top) and EQE (bottom) characteristics of DOT-PQ dendrimer/$PC_{61}BM$-blended devices (ratio 1:3 w/w).

In conclusion, we developed a facile synthesis of tetrabrominated pyrazino[2,3-*g*]quinoxaline **8** as a central building block for the synthesis of structurally defined core-functionalized π-conjugated dendrimers. Dendrimers **7** and **10** were built up via Suzuki−Miyaura cross-coupling of **8** with dendronized boronic acid esters **5** and **9** in high to moderate yields. The optoelectronic properties of dendrimers **7** and **10** clearly revealed decreased band gaps due to their donor−acceptor character and the aptitude for BHJSCs due to the well suited HOMO/LUMO energy levels. Initial testings of dendrimers **7** and **10** as p-type semiconducting component in BHJSCs gave good efficiencies of up to $\eta = 1.3\%$ which were superior to comparable all-thiophene dendrimers. Building block **8** will be further used for tailor-made synthesis of conjugated dendrimers for organic electronic applications.

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Supporting Information Available: Detailed experimental procedures, NMR and mass spectra of all new compounds, and CV measurements of **7** and **10**. Description of BHJSC device preparation and measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Cyclic voltammetry measurements were carried out in dichloromethane as solvent. Redox potentials were calculated against ferrocene/ferrocenium as external standard. For the calculation of the band gaps the following equations were used: $E_{HOMO} = (-5.1 - E_{Ox1})$ eV; $E_{LUMO} = (-5.1 - E_{Red1})$ eV.